

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number: **0 407 566 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 30.11.94 (51) Int. Cl.<sup>5</sup>: C08J 5/18, B01D 71/00

(21) Application number: 90903062.9

(22) Date of filing: 24.01.90

(96) International application number:  
PCT/US90/00498

(67) International publication number:  
WO 90/08801 (09.08.90 90/19)

(54) HIGHLY AIR PERMEABLE EXPANDED POLYTETRAFLUOROETHYLENE MEMBRANES AND PROCESS FOR MAKING THEM.

(30) Priority: 02.02.89 US 305839

(43) Date of publication of application:  
16.01.91 Bulletin 91/03

(45) Publication of the grant of the patent:  
30.11.94 Bulletin 94/48

(84) Designated Contracting States:  
AT BE CH DE DK ES FR GB IT LI LU NL SE

(56) References cited:  
EP-A- 0 106 496  
GB-A- 2 025 835  
US-A- 4 187 390

(73) Proprietor: W.L. GORE & ASSOCIATES, INC.  
551 Paper Mill Road,  
P.O. Box 9206  
Newark, Delaware 19714-9206 (US)

(72) Inventor: BACINO, John, E.  
34 White Oak Road  
Landenberg, PA 19350 (US)

(74) Representative: McCallum, William Potter et al  
Cruikshank & Fairweather  
19 Royal Exchange Square  
Glasgow G1 3AE Scotland (GB)

EP 0 407 566 B1

BEST AVAILABLE COPY

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

## Description

The present invention relates to thin expanded porous polytetrafluoroethylene products. More particularly, it relates to thin porous polytetrafluoroethylene membranes which have very large pores and so high permeabilities to air, i.e. 3.0 to 9.1 liters/min/cm<sup>2</sup> at 12.7 mm water pressure (Frazier numbers between 100 and 300). The membranes have a unique open structure and are particularly suitable for use as air or liquid filtration media, as substrates for coatings, and other uses as will be obvious to those skilled in the art.

Expanded porous polytetrafluoroethylene products are well known, as for example in US-A-3,953,566 and US-A-3,962,153. The products described therein have air permeabilities on the order of .032 metric permeability units (which corresponds to 0.02 liters/min/cm<sup>2</sup> at 12.7 mm water pressure (Frazier number 0.67). US-A-4,187,390 describes such products having air permeabilities on the order to 0.6 metric units (which corresponds to a Frazier number of 12). US-A-4,598,011 also describes such products having air permeabilities expressed as Gurley numbers of 6.5 to 27.5 seconds (which corresponds to 0.015 to 0.003 liters/min/cm<sup>2</sup> at 12.7 mm water pressure [Frazier numbers of 0.48 to 0.11]).

Heretofore, expanded porous polytetrafluoroethylene membranes with air permeabilities greater than about 2.1 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers of 70) were commercially unknown. Similarly, the production of thin membranes with densities of 0.2 g/cm<sup>3</sup> or below and porosities at or about 90% and thicknesses below 25.4 micrometers (one mil) usually led to products which were too fragile to handle.

It is desirable to provide membranes with higher air permeabilities and greater efficiencies. Typically, air filtration to achieve very low particulate contamination in the filtered air has been performed with membranes with small pores and with high efficiencies of particulate capture. Efficiency is a measure of the number of particles of a predetermined size which are prevented from penetrating a filter.

GB-A-2025835 discloses a process for producing a porous polytetrafluoroethylene body which is formed by shaping an article consisting of a mixture of PTFE powder and a lubricating agent, heating and drying the article and stretching the heated article. Stretching ratios are given between 100% to 1000% (1.1:1 to 11:1), with 1.2:1 to 8:1 being preferred.

In the computer disc drive industry, where extreme cleanliness is imperative to success, it is recognized that it is more important to reduce particulate contamination quickly by recirculating the air more rapidly through a more permeable, less efficient filter, and to get to a similar level of total contamination as one would get more slowly with a high efficiency filter. To achieve this end, polytetrafluoroethylene membranes with much higher air permeabilities than have been available heretofore were required. Commercially available porous expanded polytetrafluoroethylene membranes for filtration membranes have air permeabilities of up to 2.1 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure a (Frazier number of 70) and efficiencies of about 93% when challenged with sodium chloride (0.3  $\mu$ m particle size) aerosols at 3.2 meters/minutes (10.5 feet per minute) space velocity.

The invention provides a thin, low density, porous expanded polytetrafluoroethylene membrane having a very open structure defined by small nodes interconnected with fibrils, said membrane characterised by having a porosity equal to or greater than 90%, a density of 0.2 g/cc or less, and permeabilities to air between 3.0 and 10.7 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers of 100 and 350).

The invention further provides a process for the production of a thin low density, porous polytetrafluoroethylene membrane as described in the preceding paragraph, and having a very open structure, including the step of wetting with extrusion assisting agent a polytetrafluoroethylene membrane tape formed from coagulated polytetrafluoroethylene dispersion powder and expanding the tape by stretching while wet.

Use of this invention provides thin, porous low density expanded polytetrafluoroethylene membranes with very large pores and very high air permeabilities. The open membranes or webs have structure defined by series of rows of nodes running transversely across the membrane. The membranes of the invention have porosities equal to or greater than 95%, densities of 0.2g/cm<sup>3</sup> or less, thickness below 25.4  $\mu$ m (1 mil) and air permeabilities between 3.0 and 9.1 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (100 and 300 Frazier numbers).

To obtain the membrane of this invention it is necessary to first stretch the membrane tape while wet with extrusion aid. This is done by stretching the wet tape to at least 1.5 times and preferably 2 to 4 times its original width. It has been found that when said wet stretching is included in the process, the ability of the subsequently dried tape to longitudinally expand is markedly increased. If the stretching is done in several steps, many tapes can be expanded up to 30 times their original length. Subsequent transverse stretching to at least 1.5 times, preferably 6 to 11 times the original width. Preferably, this last stretch step is followed by sintering to amorphously lock the membrane structure providing very open diaphanous webs.

During initial longitudinal stretching, rows of nodes are formed which are substantially continuous bars of dense tightly packed particles in which nodes are connected to nodes transversely and the rows of nodes are connected to each other longitudinally by fibrils. During continued stretching, the bars of nodes form smaller individual (usually less than 10  $\mu\text{m}$ ) in the largest dimension) nodes or clumps of small nodes, which are joined to each other by fibrils and the rows of nodes are joined to each other by very long fibrils. When stretching approaches the top limits of the invention, providing membranes with flow rates of 6.1 to 10.7 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers of 200 to 350), the nodes are virtually all separated and have themselves begun to have a fibrillated structure.

It has also been found that the openness or permeability of said membranes is increased by using larger amounts of extrusion aid, up to the limit of the particular resin to provide a coherent and uniform extrudate.

There will now be described examples of membranes according to the invention.

In the Figures:-

Figure 1 is a Scanning Electron Micrograph of the membrane of Example 6 in Table II at 1000 magnifications illustrating the rows of transverse fibrillated nodes connected by bundles of fibrils and the longitudinal fibrils forming large pores;

Figure 2 is a drawing depicting the structure seen in Figure 1;

Figure 3 is a drawing depicting the equipment used for longitudinal expansion; and

Figure 4 depicts an air resistance measuring device.

The long fibrils 1 shown in Figure 2 connect the rows 2 of transverse fibrillated nodes 3 connected by bundles of fibers 4 resulting in large open pores 5.

The equipment shown in Figure 3 and used for longitudinal expansion consists of a bank 6 of feed rolls 7 and a bank 8 of take up rolls 9 through which the tape 10 is threaded, passing through heating zone 11.

The drawing of Figure 4 depicts the device used for measuring the air resistance of the membrane from which the permeability in Frazier numbers is calculated. The source of air (1) compressor feeds a receiving tank and the air flows then through a pressure regulator 3 and needle valve 4 to adjust the flow measures by flowmeter 5. A known amount of air 6 at a controlled flow rate passes into the upper stream chamber 7 which holds the sample membrane 9 sealed to the down stream chamber 10 by seals 11. The resistance of flow of the air induced by the membrane is measured in a water-filled U-tube manometer 12.

The products of this invention are thin, porous, low density membranes of expanded polytetrafluoroethylene, (preferably less than 24.5 micrometers (1 mil) in thickness) whose structures are defined by a series of rows of nodes running transversely across the membrane. These nodes appear early in the longitudinal stretching process as bars of dense, tightly packed particles; the bars can be considered to consist of nodes connected to nodes transversely and the series of bars are connected to other bars longitudinally by fibrils. After longitudinal and transverse stretching as described herein the bars have become broken up and form very small particles or clumps of particles (or small nodes) usually 10  $\mu\text{m}$  or less in the longest dimension. Preferably, the small nodes are joined to other such nodes by fibrils and bundles of fibrils and the series of rows are joined longitudinally by very long fibrils. When the stretching is carried out to provide membranes with flow rates at 3.0 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers of about 100) or above, even the nodes appear to take on a fibrillated nature.

The pores in these membranes are so large that the usual method of estimating pore size by ethanol or methanol bubble point fails. Using scanning electron micrographs and physically measuring the dimensions the majority of the pores appear to have areas of about 40  $\mu\text{m}^2$  to 200  $\mu\text{m}^2$ . Membranes of this invention have air permeabilities of 3.0 to 9.1 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (100 to 300 Frazier numbers) preferably 4.6 to 9.1 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (150-300), and filtration efficiencies of 35% to 60% at 0.3  $\mu\text{m}$  particle size.

Air permeability, as used herein, is expressed as liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers), which ordinarily means the volume of air in cubic feet (28.316 liters) passing through one square foot (929 cm<sup>2</sup>) of sample under a differential pressure of 0.50 inches (12.7mm) of water per minute. Herein, the Frazier number is a calculated value determined from the air resistance measurements described herein. The calculation is:

$$\frac{133.33}{\text{mm water resistance}}$$

$$= \text{Frazier Number}$$

Porosity as used herein is determined by the equation:

$$\text{Porosity} = 100 \frac{2.22 - \text{S.G. of sample}}{2.2}$$

5

2.2

S.G. - specific gravity

The polytetrafluoroethylene used herein is a coagulated dispersion of fine powder poly-  
 10 tetrafluoroethylene. Several such resins that have been used demonstrate that the various commercially  
 available fine powders from the several suppliers of such resins are suitable in the process. Some such  
 resins can tolerate more extrusion aid than others and still yield products within the range of permeability  
 desired. Some such resins suitable for use are Fluon (Registered Trade Mark) CD-123 and Fluon CD-1  
 15 available from ICI Americas, Inc., although there is some batch to batch variability which alters how much  
 they can be expanded. E.I. duPont de Nemours and Co., Inc., also manufacture Teflon (Registered Trade  
 Mark) fine powders that are suitable for use.

The coagulated dispersion powders are lubricated with 22 to 42 parts per hundred (pph) by weight (130  
 cc/lb to 250 cc/lb) of a hydrocarbon extrusion aid, preferably an odorless mineral spirit such as Isopar K  
 (Registered Trade Mark-made by Exxon Corp.). The lubricated powder is compressed into cylinders and  
 20 extruded in a ram extruder to form tapes. The tape is compressed between rolls to an appropriate  
 thickness, usually 127 to 254 micrometers (5 to 10 mils.). The wet tape is stretched to 1.5 to 5 times its  
 original width. The extrusion aid is driven off with heat. The dried tape is then expanded longitudinally  
 between banks of rolls in a spaced heated to a temperature that is below the polymer melting point (327°C).  
 The longitudinal expansion is repeated up to 6 times to a total expansion of at least 5 times and up to 30  
 25 times the original tape length.

In each step of longitudinal expansion, the payoff rolls can be made to rotate more slowly than the take-  
 up rolls so effecting the expansion. The tape is allowed to neck down, both transversely and in thickness  
 during the longitudinal expansion. Care must be taken to avoid splitting of the tape during these expansions.

Next, the tape, after the longitudinal expansion, is expanded transversely at a temperature that is less  
 30 than 327°C to at least 1.5 times and preferable to 6 to 11 times the width of the original extrudate while  
 restraining the membrane from longitudinal contraction. While still under constraint the membrane is  
 preferably heated to above the polymer melting point (327°C) and then cooled.

The effect of varying the amount of extrusion aid on the permeability of the final film is illustrated in the  
 examples. Briefly, increased amount of extrusion aid result in increased air permeability (or lower resistance  
 35 to air flow) in the membranes made with the same amount of expansion. Generally, for this process  
 extrusion aid levels below about 22 pph by weight (130 CC/pound) of resin are not used. The particular  
 polytetrafluoroethylene resin being used largely determines the maximum amount of extrusion aid that can  
 be used. Some resins are more tolerant to large amounts of lubricant, whereas others require less. Over-  
 lubricated powders produce non-uniform extrudates which tend to fracture during expansion.

Similarly, the permeability of the final membranes increases with increased amounts of expansion at the  
 40 same lubricant level. This too is illustrated in the examples.

It is unexpected and surprising, and contrary to previous experience, that a general purpose poly-  
 tetrafluoroethylene coagulated dispersion powder such as Fluon (Registered Trade Mark) CD-1, should  
 expand to the extent needed to provide the products of this invention. In fact, in this process, some batches  
 45 of Fluon CD-1 out perform Fluon CD-123, providing membranes with higher Frazier numbers from similarly  
 lubricated powders and similar amount of expansion than does Fluon CD-123.

The longitudinal expansion provides the row of nodes connected by nodes and some fibrils across the  
 tape and long longitudinal fibrils which connect the rows. The transverse expansion breaks or cracks the  
 clumps of nodes or bars to provide very small nodes with many fibrils connecting node to node both in the  
 50 transverse and longitudinal directions. This creates an open or porous structure.

It is this open, but strong, structure that provides the high permeability of the membranes or webs of  
 this invention, and provides an extremely thin, highly porous and very low density product, while still having  
 sufficient strength for use in filtration.

In a preferred embodiment, the polytetrafluoroethylene coagulated dispersion powder is lubricated with  
 55 140 to 190cc. of Isopar K (Registered Trade Mark) extrusion aid per 454 grams (1 pound) of resin. The  
 lubricated powder is compressed into a cylinder and extruded in a ram extruder to provide a tape. The tape  
 is compressed between rollers to between 127 to 254 micrometers (5 to 10 mils) and is stretched  
 transversely to 2 to 4 times, most preferably 3 times its original width. The lubricant is driven off by heating

to about 210°C. Longitudinal expansion is performed in an apparatus as illustrated in Figure 3. The dried tape is fed into a bank of 3 or 4 rolls which are driven at a controlled but variable speed. The tape passes through a zone heated to a temperature below the polymer melting point (327°C) preferably to 250° to 300°C and then into a second bank of 3 rolls which are driven independently of the first bank and whose speed is also variable. Expansion takes place by having the second set of rolls rotating more rapidly than the first bank. The tape is expanded longitudinally in 2 to 6 steps to a total of from 1.5 times to up to 30 times its rolled down length, depending upon the air permeability desired. During the longitudinal expansion the tape both narrows and thins due to necking. The tape is then expanded transversely at a temperature below its polymer melting point (327°C) preferably at 250° to 300° to 7.0 to 11 times its original extruded width. The transverse expansion is performed while constraining the membrane from longitudinal shrinkage. The membrane is heated to above the polymer melting point (327°C), more preferably to 360°C, and then cooled.

When performed under the aforescribed conditions, highly porous, very thin expanded polytetrafluoroethylene membranes with permeabilities to air up to 9.1 liters/min/sq.cm. at 12.7 mm water-pressure (Frazier numbers of 300) are produced.

Physical properties of a typical membrane (Example 3) produced by this invention are shown in Table I.

The products of this invention find use in air filtration equipment used in areas demanding rapid attainment of extreme cleanliness, in surgical masks, vacuum cleaner filters or bags, exhaust filters and generally in recirculating filtration equipment.

Table I

	Membrane of Example 3 Properties
Frazier Number	196 (6.0 liters/min/cm <sup>2</sup> at 12.7mm H <sub>2</sub> O)
Density (g/cc)	0.09
Porosity (%)	96
Thickness (micrometers)	9 (0.3 mils)
Water Entry Pressure (kPa)	2.5 (0.36 p.s.i)
Filtration efficiency with 0.3 µm aerosol, %	46.9
Matrix Tensile Strength (MPA)*	146.8 ± 20.7 (21292 ± 3002 p.s.i)

\*Matrix tensile strength is determined by dividing the maximum force to break by the cross sectional area of the sample and multiplying by the ratio of the specific gravity of the solid polymer divided by the specific gravity of the sample material.

#### Thickness

Thickness is determined from one ply of membrane 12.7 cm x 12.7 cm (5 inches by 5 inches) square using shim stock so as not to compress the membrane while measuring thickness with calipers.

#### Density

Density is determined by weighing the 12.7 cm x 12.7 cm (5 inch by 5 inch) square membrane used to determine thickness and calculating the density.

#### Tensile Strength

Tensile strength is determined by the method described in ASTM D992.

#### Water Entry Pressure

Water entry pressure was measured by mounting a membrane sample on a test plate taking care not to damage the membrane. The sample was then placed over a water filled J-tube was then pressurized in small increments, waiting 30 seconds after each change of pressure and watching for the first signs of water break through in the center of the film (to avoid erroneous results from damaged edges). The pressure at break through was recorded as the water entry pressure. A minimum of four samples were tested and the

average of the results was reported.

#### Air Permeability

5 Air permeability is calculated using the resistance to flow measurement.

For the purposes of this patent, "resistance" is defined, generally, as the differential pressure across a sheet of air filter media just sufficient to cause air to flow through the sheet at a chosen air velocity, and more specifically, as the differential pressured measured in mm of water column causing an air velocity of 3.2 m/min.

10 Resistance is measured as follows: a hollow test chamber is clamped about a sheet of media such that the sheet partitions the chamber interior into two separate compartments, and such that the junction of the chamber walls and the sheet is throughout its perimeter well sealed. This sheet has some known area exposed to the chamber interior as defined by the inner perimeter of the seals.

The chamber compartment that is on one side of the sheet is freely vented to the atmosphere. On the other side of the sheet, the other compartment is sealed to some source of controlled air flow. This source is provided by an air compressor, a receiving tank, a pressure regulator, a needle valve, and a flowmeter.

The air source is adjusted to deliver the correct air flow, equal to the aforementioned known sheet area multiplied by the desired air velocity (and therefore having the correct dimensions of volume per unit time). For example, if the sheet area defined by the seals is 0.15 m<sup>2</sup>, the correct flow would be:

$$20 \quad (0.15 \text{ m}^2) \times (3.2 \text{ m/min}) = (0.48 \text{ m}^3/\text{min})$$

A sensitive differential pressure sensing device, such as a water-filled "U" tube or an electronic transducer, is connected to the two chamber compartments such that it registers the pressure differential across the sheet.

The sheet sample's resistance is measured by sealing the sheet between chamber parts, establishing the correct air flow through the chamber and sheet, and detecting the resultant differential pressure.

Moreover, additional optional precautions to improve the accuracy of measurement include the chamber being double-walled and the seals doubled, such that a guard zone separately surrounds the known sheet area, and this surrounding space plumbed to transport additional air identically through the guard zone, such that the inner seal which defines the known area envoys equal pressures within and without, and zero leakage is guaranteed from the critical inner chamber.

Also, the flowmeter is a precalibrated laminar flow elements, whose linear differential pressure output is read by the same pressure instrument through valving, such that scaling and viscosity (temperature) errors are to a first order cancelled and the determination is in fact rationmetric.

The ratio of absolute pressures is measured between the flowmeter and the downstream chamber compartment, and an ideal gas law correction is applied, such that a volumetric flow is rightly determined at the downstream face of the sheet.

Using resistance values in mm water pressure across the sample, Frazier numbers are calculated by:

$$40 \quad \frac{133.33}{\text{mm H}_2\text{O}} = \text{Frazier number}$$

#### Efficiency Testing

50 The filter efficiency testing is done using a similar apparatus/housing as the resistance test. A well mixed, sodium chloride aerosol in an air stream with a known velocity is directed thru a sample of air filter media. A small sample is taken of the challenge air stream and the penetrating air stream. The sample are channelled thru to dual laser particle counters which give an accurate count of the sodium chloride particles in each air stream. A penetration value is the ratio of the counts of particles larger than 0.3 μm in the penetrating air stream/counts of particles larger than 0.3 μm in the challenge air stream. The % efficiency value is 100 minus percent penetration.

### EXAMPLES

The table illustrates the effect of different hydrocarbon extrusion aid lubricant levels and of stretch lengths on the air permeabilities of the membranes.

5     Examples 2 and 3 demonstrate the degree of repeatability of the process. Examples 1 and 2 demonstrate the effect of higher longitudinal expansion at constant extrusion aid levels on air permeability.

#### Example 5

10     Polytetrafluoroethylene fine powder, Fluono (Registered Trade Mark) CD-1 (available from ICI Americas, Inc.) was blended with Isopar K (available from Exxon Corp.) at the rate of 28.5 pph by weight (170cc of Isopar K/pound) of fine powder. The lubricate powder was compressed into a cylinder and was ram  
15     1/2 mils) and was stretched transversely to 2.4 times its original width. The Isopar K was driven off by heating to 210°C. The dry tape was expanded longitudinally between banks of rolls in a zone heated to 250°C. The ratio speeds of the second bank of rolls to the first bank of rolls was 1.5/1 in the first pass and 5.8/1, 1.5/1, and 1.5/1 in subsequent passes for a total of 19.6 times total longitudinal expansion. The tape was heated to 250°C and transversely expanded to 7.4 times the width of the extrudate while constrained  
20     from shrinkage and then to 360°C while still constrained. The membrane had a density of 0.2 g/cm<sup>3</sup>, its air permeability was 4.75 liters/min/cm<sup>2</sup> at 12.7 mm water-pressure (a Frazier number of 156) and it had a efficiency of 66.3% of 0.3 µm particles.

#### Examples 1-4 and 6

25     Other examples were made using the above procedure with various polytetrafluoroethylene coagulated dispersion powders. The only operating variables were the amount of extrusion aid used and the total amount of longitudinal expansion. These operating variables are shown in Table II with the air resistance, the air permeability in Frazier numbers and the percent efficiency in capturing 0.3 µm and larger particles  
30     for each sample.

35

40

45

50

55

**TABLE II**  
**Manufacture of Membranes with a Broad**  
**Range of Air Permeability\***

Example	Lubricant cm <sup>3</sup> /454g	Longitudinal Expansion (total)	Resistance mm H <sub>2</sub> O	Frazier Numbers	l/min/cm <sup>2</sup> at 12.7 mm water- Pressure	Efficiency
1	160	22.2	.95	140	4.23	49.5
2	160	28.0	.69	202	6.12	55.
3	160	28.0	.68	196	5.98	46.9
4	175	25.0	.45	296	9.03	34.4
5	170	19.6	.85	156	4.75	66.3
6	170	27.0	1.21	110	3.35	84.5
Comparison**	200	8.7	Failed to Expand			

\*Air permeabilities as expressed by resistance to air flow in mm H<sub>2</sub>O and 10.5 fpm space velocity and as Frazier numbers

\*\*At 200 cm<sup>3</sup>/454g lubricant, the material could not be expanded beyond 8.7/1 and produced non-uniform membrane when expanded transversely.

#### Claims

1. A thin, low density, porous expanded polytetrafluoroethylene membrane having a very open structure defined by small nodes interconnected with fibrils, said membrane characterized by having a porosity equal to or greater than 90%, a density of 0.2 g/cm<sup>3</sup> or less and an air permeability of 3.0 to 10.7



litres/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers of 100 and 350).

2. The membrane of claim 1, wherein the majority of the nodes are arranged in series of generally aligned parallel rows across the membrane, and are connected node to node by fibrils and bundles of fibrils and the rows are connected to each other by long fibrils.
3. The membrane of claim 1 wherein the membrane is a film of a thickness of less than 25.4 micrometres (1 mil.).
4. A membrane of claim 2 wherein the membrane is a film of a thickness of less than 25.4 micrometres (1 mil.).
5. The membrane of claim 4 wherein the permeability to air is between 4.6 and 9.1 litres/min/cm<sup>2</sup> at 12.7 mm water-pressure (Frazier numbers of 150 to 300).
6. An air filtration device containing a membrane of claim 1 as the filter.
7. An air filtration device containing a membrane of claim 2 as the filter.
8. A process for the production of a thin low density, porous polytetrafluoroethylene membrane as claimed in claim 1 having a very open structure, including the step of wetting with extrusion assisting agent a polytetrafluoroethylene membrane tape formed from coagulated polytetrafluoroethylene dispersion powder and expanding the tape by wet-stretching.
9. A process as claimed in claim 8 wherein a further stretching step is carried out subsequent to the drying out of said extrusion assisting agent.

#### Patentansprüche

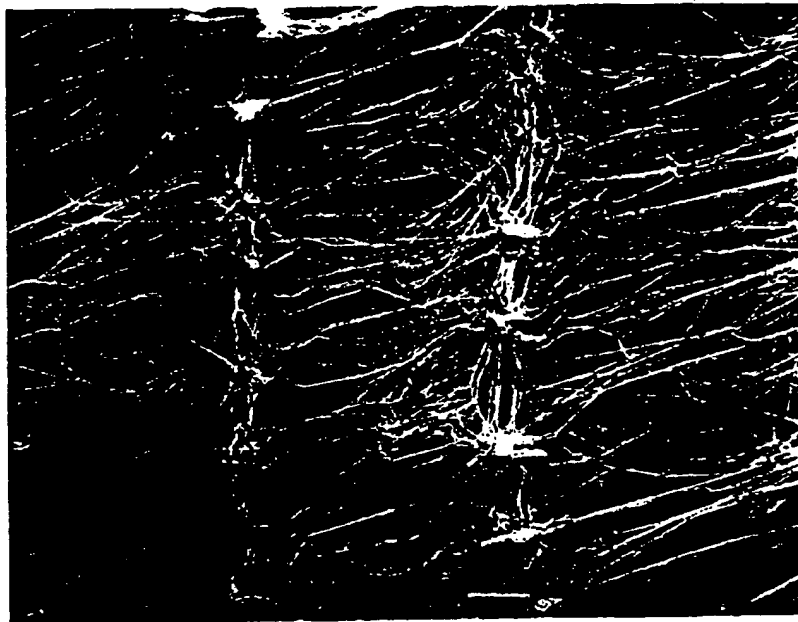
1. Eine dünne, eine niedrige Dichte aufweisende, poröse, expandierte Polytetrafluorethylen-Membran mit einer sehr offenen Struktur, die durch kleine Knoten gebildet ist, die untereinander durch Fibrillen verbunden sind, wobei die genannte Membrane **gekennzeichnet ist** durch: eine Porösität gleich oder größer als 90 %, eine Dichte von 0.2 g/cm<sup>3</sup> oder geringer und eine Luftdurchlässigkeit von 3,0 bis 10,7 Liter/min/cm<sup>2</sup> bei 12.7 mm Wasserdruck (Frazier-Nummern von 100 und 350).
2. Die Membrane nach Anspruch 1, bei welcher die Mehrzahl der Knoten reihenweise in der Form von im wesentlichen miteinander ausgerichteten, parallelen Reihen quer über die Membrane angeordnet ist, wobei Knoten mit Knoten durch Fibrillen und Bündel von Fibrillen verbunden ist und wobei die Reihen miteinander durch lange Fibrillen verbunden sind.
3. Die Membrane nach Anspruch 1, bei welcher die Membrane eine Folie mit einer Stärke von weniger als 25.4 Mikrometer (1 mil.) ist.
4. Eine Membrane nach Anspruch 2, bei welcher die Membrane eine Folie mit einer Stärke von weniger als 25.4 Mikrometer (1 mil.) ist.
5. Die Membrane nach Anspruch 4, bei welcher die Durchlässigkeit für Luft zwischen 4,6 und 9,1 Liter/min/cm<sup>2</sup> bei 12,7 mm Wasserdruck (Frazier-Nummern von 150 bis 300) liegt.
6. Eine Luftfiltrations-Vorrichtung, welche eine Membran gemäß Anspruch 1 als das Filter enthält.
7. Eine Luftfiltrations-Vorrichtung, welche eine Membran gemäß Anspruch als das Filter enthält.
8. Ein Verfahren zur Herstellung einer dünnen, eine niedrige Dichte aufweisenden, porösen Polytetrafluorethylen-Membran, wie in Anspruch 1 beansprucht und die eine sehr offene Struktur aufweist, umfassend den Schritt des Benetzens eines Polytetrafluorethylen-Membran-Bandes, das aus einem koagulierten Polytetrafluorethylendispersions-Pulver gebildet ist, mit einem die Extrusion unterstützenden Mittel, und des Expandierens des Bandes durch Naß-Recken.

9. Ein Verfahren, wie in Anspruch 8 beansprucht, bei welchem ein weiterer Schritt des Reckens im Anschluß an das Austrocknen des genannten die Extrusion unterstützenden Mittels ausgeführt wird.

# Revendications

- 5 1. Une membrane en polytétrafluoroéthylène expansé et poreux, mince et de faible densité, présentant une structure très ouverte définie par de petits noeuds entrelacés par des fibrilles, ladite membrane étant caractérisée en ce qu'elle présente une porosité égale ou supérieure à 90 %, une densité égale ou inférieure à 0,2 g/cm<sup>3</sup>, et une perméabilité à l'air comprise entre 3,0 et 10,7 litres/minute/cm<sup>2</sup> à une  
10 pression d'eau de 12,7 mm (nombres de Frazier compris entre 100 et 350).
2. La membrane selon la Revendication 1, dans laquelle la majorité des noeuds est disposée en séries de rangées généralement alignées parallèlement en travers de la membrane, et dont les noeuds sont  
15 reliés entre eux par des fibrilles et des bottes de fibrilles, et les rangées sont reliées entre elles par de longues fibrilles.
3. La membrane selon la Revendication 1, dans laquelle la membrane est un film dont l'épaisseur n'excède pas 25,4 micromètres (1 millième de pouce).
- 20 4. Une membrane selon la Revendication 2, dans laquelle la membrane est un film dont l'épaisseur n'excède pas 25,4 micromètres (1 millième de pouce).
5. La membrane selon la Revendication 4, dans laquelle la perméabilité à l'air est comprise entre 4,6 et 9,1 litres/minute/cm<sup>2</sup> à une pression d'eau de 12,7 mm (nombres de Frazier compris entre 150 et 300).
- 25 6. Un dispositif de filtration de l'air composé d'une membrane selon la Revendication 1 faisant office de filtre.
7. Un dispositif de filtration de l'air composé d'une membrane selon la Revendication 2 faisant office de  
30 filtre.
8. Un procédé pour la fabrication d'une membrane en polytétrafluoroéthylène poreux, mince et de faible densité, telle que revendiquée à la Revendication 1, présentant une structure très ouverte, et comprenant les étapes consistant à humidifier à l'aide d'un agent d'aide à l'extrusion une bande de  
35 membrane en polytétrafluoroéthylène formée à partir d'une poudre de dispersion coagulée de polytétrafluoroéthylène, et à expanser la bande par étirage humide.
9. Un procédé selon la Revendication 8, dans lequel on conduit une étape supplémentaire d'étirage suite à l'assèchement dudit agent d'aide à l'extrusion.
- 40
- 45
- 50
- 55

*FIG. 1*



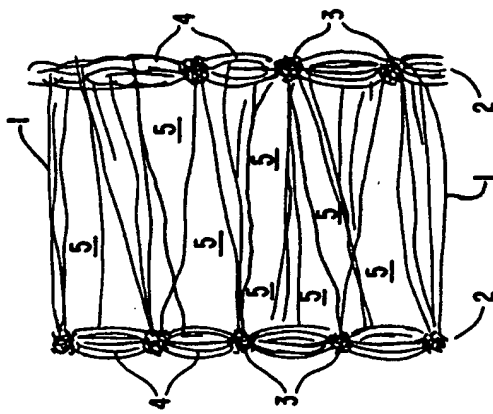


FIG. 2

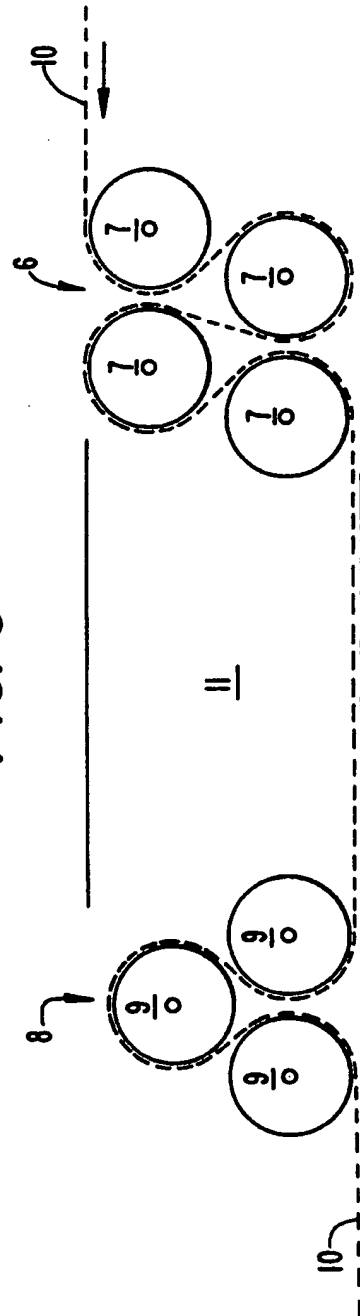
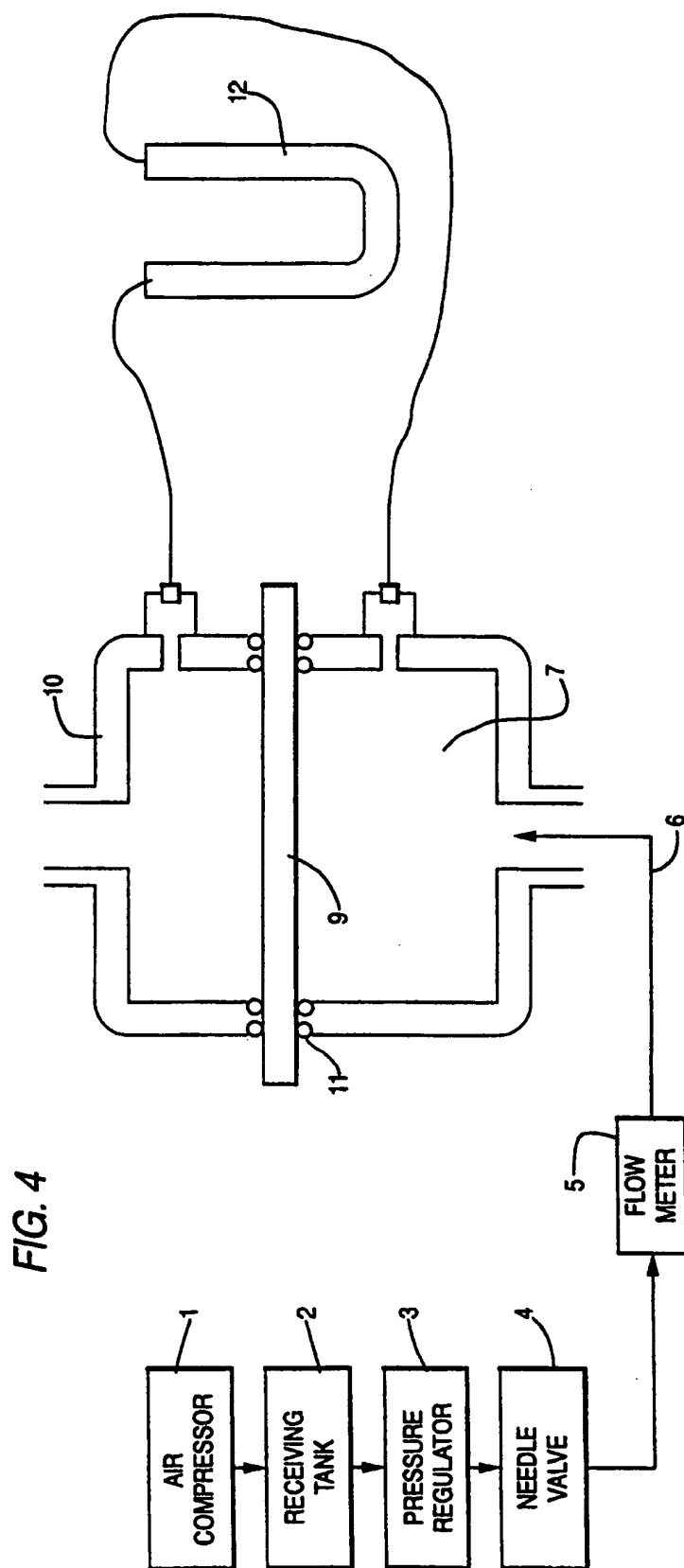


FIG. 3



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**